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(54) Battery separator

(57) A siliceous filler-reinforced microporous polymeric material battery separator wherein the siliceous filler comprises agglomerates of substantially hollow spherical particles of amorphous, precipitated silica having a predominant hollow spherical particle size of between  $5 \times 10^{-6}$  mm and  $5 \times 10^{-3}$  mm (between 0.005 and 5.0 microns), the siliceous filler having a surface area of between about 50 and 200 square metres per gram, and an oil absorption of from about 150 to 300 millilitres per 100 grams of filler.

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## SPECIFICATION

## Battery separator

5 The present invention relates to a siliceous filler-containing battery separator.

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In commonly used electric storage batteries, such as the well-known 12-volt battery employed in automobiles, separators are placed between battery plates of opposite polarity to prevent the two plates from touching each other and causing an electrical short. The separator is typically a microporous article fabricated from a polymeric material, e.g., natural or synthetic rubber, or a polyolefin. The separator may have a backing material of, for example, a non-woven web. The pore size of the microporous separator should be as small as possible since this reduces the danger of active materials being forced through or growing through the separator, thereby causing an electrical short.

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The separator should also have a low electrical resistance in order to maximize the power output from the battery. Lower electrical resistance can be obtained by reducing the overall thickness of the separator, e.g., the thickness of the backing material. However, thinner separators are more subject to corrosion and other physical factors affecting the service life of the separator.

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Certain siliceous fillers have been used to prepare microporous battery separators. For example, U.S. Patent Specification No. 2,302,832 describes the use of a silica hydrogel in a rubber binder; U.S. Patent Specification No. 3,351,495 describes synthetic and natural zeolites, precipitated metal silicates, such as calcium silicate, and silica gels as the inorganic filler and extender for separators of high molecular weight polyolefins; and U.S. Patent Specifications Nos. 3,696,061, 4,226,926, and 4,237,083 describe the use of finely divided, precipitated amorphous silica, such as Hi-Sil 233 (Hi-Sil is a Trade Mark), in microporous battery separators.

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Typically, amorphous precipitated silica filler is used to introduce porosity into the polymeric material utilized to form the battery separator. This siliceous filler is highly absorbent and can absorb a substantial quantity of an aqueous or organic liquid while remaining free flowing. In practice, the amorphous precipitated silica is loaded with the liquid and then blended with the polymeric material. The liquid absorbed by the silica filler is subsequently removed to impart porosity to the polymer.

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It has now been discovered that certain precipitated siliceous fillers permit the fabrication of battery separators having reduced electrical resistance compared to separators prepared with conventional amorphous precipitated silica fillers, such as the aforementioned Hi-Sil 233 silica filler. In the present invention, a siliceous filler composed of agglomerates of substantially hollow spherical precipitated siliceous particles is used to prepare microporous polymeric battery separators.

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According to the present invention there is provided a siliceous filler-reinforced microporous polymeric material battery separator wherein the siliceous filler comprises agglomerates of substantially hollow spherical particles of amorphous, precipitated silica having a predominant hollow spherical particle size of between  $5 \times 10^{-6}$  mm and  $5 \times 10^{-3}$  mm (between 0.005 and 5.0 microns), the siliceous filler having a surface area of between about 50 and 250 square metres per gram, and an oil absorption of from about 150 to 300 millilitres per 100 grams of filler.

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The siliceous filler used in the present invention differs from the conventional precipitated silica pigment described, for example, in U.S. Patent Specification No. 4,226,926 by the substantially hollow and spherical character of the ultimate particles of the filler.

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In accordance with the present invention, between about 10 and about 90 weight percent, basis the polymeric material, of substantially hollow, spherical precipitated siliceous filler is usually used to produce reinforced microporous polymeric battery separators. More particularly, between about 20 and about 75, especially between 30 and 60, weight percent of the siliceous filler is so used.

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This siliceous filler is composed of agglomerates of substantially hollow spherical particles having a predominant hollow particle size (diameter) of between  $5 \times 10^{-6}$  mm and  $5 \times 10^{-3}$  mm (between 0.005 and 5.0 microns), preferably between  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$  mm (between 0.01 and 1.0 microns), more preferably between  $1 \times 10^{-5}$  and  $2 \times 10^{-4}$  mm (between 0.01 and 0.20 microns). The siliceous filler is further characterized by a surface area of between about 50 and 250 square metres per gram ( $m^2/gram$ ), preferably between 75 and 200  $m^2/gram$ , and an oil absorption of from about 150 to 300, preferably from about 200 to 300, and more preferably from about 230 to 270, ml of oil per hundred grams of siliceous filler. The surface area of the filler can be determined by the method of Brunauer, Emmett, and Teller, J. Am. Chem. Soc., 60, 309 (1938). This method, which is often referred to as the BET method, measures the absolute surface area of a material by measuring the amount of gas adsorbed under special conditions of low temperature and pressure. The BET surface areas reported in the Examples hereinbelow were obtained using nitrogen as the gas adsorbed and liquid nitrogen temperatures ( $-196^\circ C$ ) and at a 0.2 relative pressure. Oil absorption values are the volume of dibutylphthalate oil necessary to wet 100 grams of the pigment. These values can be obtained using the method described in ASTM D2414-65.

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The siliceous filler can be prepared in accordance with the process described in U.S. Patent Specification No. 3,129,134. In accordance with the process therein described, the pigment is produced by precipitating water insoluble siliceous product from an aqueous siliceous solution in the presence of finely-divided particles of a water insoluble inorganic salt, e.g., calcium carbonate - especially inorganic salts of acids, the anhydride of which is normally gaseous, for example, the inorganic salts of carbonic acid. The

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water insoluble inorganic salt is then substantially removed from the resulting insoluble siliceous precipitate by treating the precipitate with acid, e.g., hydrochloric acid. This treatment converts the cation of the insoluble inorganic salt into a water-soluble salt of the treatment acid and liberates the anion of the salt as a gas. Thus, treatment of calcium carbonate solids in the silica product slurry with hydrochloric acid, produces calcium chloride as the soluble salt and carbon dioxide (or carbonic acid).

More particularly, the siliceous fillers can be prepared by precipitating siliceous product in a slurry of finely-divided water-insoluble carbonate salt, most notably calcium carbonate. The particle size of the calcium carbonate or other similar water insoluble salt of carbonic acid in the slurry should preferably approximate the desired hollow spherical particle size of the precipitated siliceous pigment to be used to prepare the battery separator. The calcium carbonate can be preformed and slurried in the aqueous medium in which the precipitation is accomplished. Alternatively, the calcium carbonate can be prepared, *in situ*, by the reaction of calcium chloride with sodium carbonate in the aqueous medium in which the precipitation is accomplished. Products produced utilizing insoluble carbonate salts formed *in situ* in the reaction vessel are generally smaller in hollow spherical particle size than those obtained using slurries of preformed water insoluble carbonate salts.

From the physical appearance of the filler, i.e., the substantial absence of water insoluble siliceous material in the core of the particles, the foregoing method apparently precipitates water insoluble siliceous material upon the surface of the finely-divided water-insoluble carbonate salts, e.g., calcium carbonate particles. This carbonate particle is subsequently converted e.g., by acid treatment to water-soluble components, thereby leaving a substantially hollow, spherical silica particle.

The method of precipitating the water insoluble siliceous material from solution described in U.S. Patent Specification No. 3,129,134 may include partially neutralizing with hydrochloric acid (or like neutralizing agent) the aqueous solution of alkali metal (e.g., sodium) silicate. The extent of this partial neutralization is such that the resulting aqueous solution will, upon standing (sometimes for but a very brief duration), precipitate water insoluble siliceous material from the solution. Prior to developing such siliceous precipitate, precipitation of the pigmentary siliceous material may be induced by introducing into the solution a precipitate-inducing soluble inorganic metal salt, such as calcium chloride and/or sodium chloride.

The substantially hollow, spherical siliceous filler (after removal of the water insoluble inorganic salt) is a finely-divided flocculated amorphous precipitated siliceous filler. The filler is in the form of flocs or agglomerates of quite small particles of siliceous material. The number average spherical particle size is below about  $5 \times 10^{-4}$  mm (0.5 micron) in diameter and usually less than  $3 \times 10^{-4}$  mm (0.3 micron) in diameter but rarely less than  $1 \times 10^{-5}$  mm (0.01 micron) in diameter. A multiplicity of these small particles are agglomerated together without complete loss of their individual identities providing the flocculated state of the filler. Flocs can range upwards of 0.04 mm (40 microns) in size, as measured at their longest dimension.

The degree to which these flocs persist (are not degraded into smaller flocs) when the filler is subjected to mechanical action, i.e., milling, can vary. However, even those fillers which have their average floc size altered by mechanical means still retain the flocculant characteristic. This flocculated state appears predominantly in the form of three-dimensional clusters, which may be likened to bunches of individual hollow grapes in which the particles in the floc are denoted by the individual hollow grapes and the floc is represented by the cluster.

An important feature of these precipitated siliceous fillers is the character of the ultimate particles. Such particles are composed of an optically dense outer shell (shell-like structure) of siliceous material. The interior volume enclosed or within the shell is of much lower optical density, e.g., below the optical density of water-insoluble precipitated siliceous material under the high magnification of an electron microscope. The ultimate particles appear almost bubble-like and spheroidal with the difference in optical density between the inner and outer volumes giving them the appearance of hollow particles.

Fluids, e.g., gases or liquids, may occupy the interior volumes of the spherical particles, the dimensions of which are defined by the inner surface of the siliceous shell of the particle. When well dried, little of any liquid, such as water, normally occupies or fills the interior volume. Typically, the siliceous shell encloses or encases completely the less optically dense interior. However, the shell is sufficiently porous to allow removal of the water-insoluble carbonate salt. That is, the shell is predominantly continuous (but porous) - at least to the extent that when the interior volume is a fluid, it is possible to remove or replace the fluid. Larger particles may have a discontinuous shell due to the non-uniform coating of large particles of the carbonate salt or the coating of aggregates of carbonate salt particles, i.e., non-dispersed individual carbonate salt particles. It is believed that the porosity of the shell is composed of indirect pathways from the outside to the inside of the shell circumventing the ultimate particles of siliceous material that make up the shell.

Chemically, the siliceous fillers have a substantial  $\text{SiO}_2$  content, usually at least 50 percent by weight  $\text{SiO}_2$  on an anhydrous basis. Also commonly present are one or more metals, usually as their metal oxides, including frequently an alkaline earth metal oxide such as calcium oxide. The hollow spherical precipitated particles desirably contain less than 2 weight percent of the alkaline earth metal (measured as the oxide) for use in battery separators. Preferably, the alkaline earth metal content is less than 1 weight percent, more preferably less than 0.5 weight percent and most preferably less than 0.1 weight percent.

The alkaline earth metal content of the siliceous filler can be reduced by treating the precipitated filler with sufficient acid to convert all of the alkaline earth metal to soluble salt and by thoroughly washing of the filler (after acid treatment and before drying).

After drying, the siliceous filler is white, fluffy, pulverulent and dry to the touch. Despite appearing dry, the filler normally contains water, e.g., between about 2 and 8 percent 'free water' by weight. Free water is that water which is removed from the filler by heating at 105°C for 24 hours. The pigment also contains 'bound water', which refers to that water removed by heating the filler at ignition temperature, i.e., 1000°C to 1200°C for an extended period, e.g., 24 hours. Bound water can constitute between about 2 and 6 percent of the filler.

The polymeric material into which the siliceous filler is incorporated to prepare the microporous battery separator can be any of the conventional natural and synthetic polymeric materials conventionally used to fabricate battery separators. Among such materials, there can be mentioned natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, polyisoprene, high molecular weight olefins such as polyethylene, polypropylene, polybutene, ethylene-propylene copolymers, ethylene-butene copolymers, propylene-butene copolymers, ethylene-propylene-butene copolymers, polyvinyl chloride and vinyl chloride-vinyl acetate copolymers. Mixtures of such materials have also been used to prepare battery separators.

Other conventional materials added to the polymeric material, such as plasticizers, antioxidants, wetting agents, carbon black and curing agents, e.g., sulfur, for rubbery polymeric materials may also be added to the composition used to prepare the battery separator.

Battery separators incorporating the above-described hollow spherical siliceous filler can be prepared in accordance with known techniques for preparing such articles. A typical procedure for preparing a battery separator utilizing a curable rubber is described in U.S. Patent Specification No. 4,226,926, wherein the siliceous filler is rehydrated to levels of between 65 and 75 percent by admixing the siliceous filler with water. The resulting free flowing rehydrated silica powder is admixed with the polymeric material, e.g., in a Banbury mixer. Thereafter, the mixture (including any additional additives required for curing the polymeric particle) is milled on a 2-roll mill to produce a milled sheet. The milled sheet is soaked in hot water and then calendered for contours. Optionally a backing such as paper or a heat-bonded mat is added to the milled sheet. The calendered sheet is then cut into appropriate sizes.

Another similar procedure is described in U.S. Patent Specification No. 3,351,495 wherein the polymeric material, e.g., a polyolefin having a molecular weight of at least 300,000, is blended with the inert filler, e.g., silica, and a plasticizer. The blend, which may also contain conventional stabilizers or antioxidants, is moulded or shaped, e.g., by extrusion, calendering, injection moulding or compression, into sheets. Plasticizer and/or filler is removed from the sheet by soaking the sheet in a suitable solvent, e.g., chlorinated hydrocarbons for a petroleum oil plasticizer and water, ethanol, acetone, etc. for a polyethylene glycol plasticizer.

The present invention will now be more particularly described in but is in no manner limited to the following Examples.

#### 40 Example I

15 litres of an aqueous solution of sodium silicate  $[\text{Na}_2\text{O}(\text{SiO}_2)_{3.18}]$  containing 20 grams per litre  $\text{Na}_2\text{O}$  was fed at the rate of 0.5 litres per minute to one arm of a tee tube. To the other arm of the tee tube, was fed 15 litres of an aqueous solution of hydrochloric acid containing 11.8 grams per litre  $\text{HCl}$  at a rate of 0.5 litres per minute. The resulting partially acidified sodium silicate solution was charged to the upper portion of a suitable reaction vessel. Added simultaneously to the upper portion of the reaction vessel through an inlet tube was 15 litres of a salt solution containing 0.48 moles per litre of calcium chloride and 0.37 moles per litre of sodium chloride at a rate of 0.5 litres per minute. Also added to the reaction vessel through an inlet tube adjacent to the salt solution inlet tube was 15 litres of an aqueous solution containing 0.16 moles per litre of sodium carbonate at a rate of 0.5 litres per minute. The reactant streams had a temperature of about 23°C. The reaction mixture collected for the first 4 minutes was discarded. The remaining reaction mixture slurry was transferred to a polyethylene lined vessel. This slurry was neutralized to a pH of 2.0 with 1600 millilitres of 6 Normal hydrochloric acid. The acidified slurry was agitated with an air stirrer for 15 minutes and the pH of the slurry readjusted to 7.5 over 15 minutes with 1380 millilitres of 2.5 Normal sodium hydroxide. The slurry was heat aged at 105°C in an oven overnight. Thereafter, the slurry was removed from the oven and filtered. The filter cake was washed with 72 litres of distilled water to wash the cake free of chloride ion. The filter cake was broken-up, placed in stainless steel trays and dried overnight in an oven at 105°C. The dried pigment was removed from the oven, rehumidified and micropulverized through a 0.508 mm (0.020 inch) round screen.

Optical microscopic examination of the micropulverized material revealed that relatively large calcium carbonate particles were still present in the product. The amount of calcium present in the product (measured as calcium oxide) was found by chemical analysis to be 4.49 percent.

The product was reslurried in 10-12 litres of distilled water and sufficient 6 Normal hydrochloric acid added to the slurry to lower the pH to 2.0. The slurry was stirred for four hours while maintaining the pH at 2.0. A total of 475 millilitres of hydrochloric acid was added to the slurry. Thereafter, the slurry was neutralized with 630 millilitres of 2.5 Normal sodium hydroxide to raise the pH of the slurry to 7.65. The

slurry was filtered and the filter cake washed with 24 litres of distilled water. The washed filter cake was dried overnight at 105°C in an oven and thereafter micropulverized through a 0.508 mm (0.020 inch) round screen. The micropulverized product was rehumidified by exposure to ambient air over a weekend.

The resulting product was submitted for surface area and oil absorption determinations, and elemental X-ray analysis. Results are tabulated in the Table hereinbelow.

#### Example II

18 litres of an aqueous solution of sodium silicate  $[\text{Na}_2\text{O}(\text{SiO}_2)_{3.16}]$  containing 10.5 grams per litre  $\text{Na}_2\text{O}$  was fed at the rate of 0.5 litres per minute to one arm of a tee tube. To the other arm of the tee tube was fed 18 litres of hydrochloric acid containing 0.187 grams per litre  $\text{HCl}$  at a rate of 0.5 litres per minute. Simultaneously, 36 litres of a salt solution (calcium chloride plus sodium chloride) containing 57 grams/litre of Camel-Wite Super ground calcium carbonate of approximately 3 micron particles were added to the reaction vessel (Camel-Wite Super is a Trade Mark). The salt solution contained 0.169 moles per litre of calcium chloride and 0.128 moles per litre of sodium chloride. The salt slurry was introduced into the reaction zone at a rate of 1.0 litre per minute. The temperature in the reaction vessel was about 18°C. The first 4-1/2 minutes of slurry produced was discarded and thereafter the resulting slurry collected. The pH of the product slurry after addition of all the reactants was 9.0. The pH of the slurry was adjusted to 2.0 with 6.0 litres of 6 Normal hydrochloric acid. The acidified slurry was stirred for 20 minutes and thereafter the pH adjusted to 8.0 with 2520 millilitres of 2.5 Normal sodium hydroxide. The resulting slurry was heat aged overnight at 105°C.

The aged slurry was removed, vacuum filtered and the filter cake washed with 112 litres of distilled water. The filter cake was broken-up and dried overnight in an oven at 105°C. The dried product was rehumidified and then micropulverized through a 0.508 mm (0.020 inch) round screen.

Optical microscopic examination of the milled pigment showed large calcium carbonate particles still present in the sample. The amount of calcium present (measured as calcium oxide) was found to be 13.3+ weight percent  $\text{CaO}$ . Accordingly, the product was reslurried in 10 to 12 litres of distilled water and 960 millilitres of 6 Normal hydrochloric acid added to the slurry to reduce the pH to 2.0. The acidified slurry was stirred for 4 hours and thereafter 310 millilitres of 2.5 Normal sodium hydroxide added to raise the pH of the slurry to 7.70. The neutralized slurry was filtered and the filter cake washed with 32 litres of distilled water. The filter cake was broken-up and dried overnight in an oven at 105°C. The dried pigment was micropulverized through a 0.508 mm (0.020 inch) round screen. The resulting product was submitted for surface area and oil absorption determinations, and elemental X-ray analysis. Results are tabulated in the Table hereinbelow.

#### Example III

In a manner similar to Example I, 36 litres of an aqueous solution of sodium silicate  $[\text{Na}_2\text{O}(\text{SiO}_2)_{3.06}]$  containing 20 grams per litre  $\text{Na}_2\text{O}$  was charged at a rate of 0.5 litres per minute into one arm of a tee tube. Through the other arm of the tee tube was charged 36 litres of hydrochloric acid containing 11.8 grams per litre at a rate of 0.5 litres per minute. The concentration of the calcium chloride/sodium chloride salt solution and sodium carbonate solution were the same as in Example I except that 36 litres of each solution were introduced into the reaction vessel at a rate of 0.5 litres per minute. The temperature within the reaction vessel was about 23-24°C. The resulting product slurry had a pH of 9.15. The pH of the slurry was adjusted to 2.0 with 3.9 litres of 6 Normal hydrochloric acid and stirred for 3 hours at that pH. Subsequently, the acidified slurry was neutralized to a pH of 7.8 with 2.4 litres of 2.5 Normal sodium hydroxide. The neutralized slurry was aged overnight in an oven at 105°C and the aged slurry filtered and washed with 96 litres of distilled water. The washed filter cake was dried overnight in a 105°C oven. The dried product was rehumidified at room temperature and micropulverized (hammer milled) through a 0.254 mm (0.01 inch) screen.

The resulting product was submitted for X-Ray elemental analysis and surface area and oil absorption determinations. Results are tabulated in the Table hereinbelow.

#### Example IV

The procedure of Example II was followed utilizing 18 litres of the aqueous sodium silicate solution described in Example III. The sodium silicate solution was partially neutralized with 18 litres of hydrochloric acid containing 12.9 grams per litre of  $\text{HCl}$  charged at a rate of 0.5 litres per minute. 36 litres of a salt solution containing 0.65 moles per litre calcium chloride and 0.51 moles per litre sodium chloride was introduced into the reaction vessel at a rate of 1 litre per minute. The salt solution contained 0.57 moles (57 grams) per litre of preformed calcium carbonate having an average particle size of 0.75 microns. The temperature in the reaction vessel was about 19°C. The pH of the resulting slurry following addition of all the reactants was 8.6. The pH of the slurry was adjusted to 2.0 with 4.82 litres of 6 Normal hydrochloric acid and the acidified slurry was stirred for 4 hours at a pH of 2. Subsequently, the aged acidified slurry was neutralized with 1.34 litres of 2.5 Normal sodium hydroxide to a pH of 7.8. The neutralized slurry was aged overnight at 105°C and subsequently filtered. The filter cake was washed with 128 litres of distilled water and the washed filter cake dried overnight in a 105°C oven. The dried product was rehumidified at room temperature and micropulverized through a 0.254 mm (0.01 inch) screen. The

milled product was submitted for physical and chemical analysis. Results are tabulated in the following Table.

TABLE

Example No.	Particle Size* Range, mm (microns)	Surface Area, m <sup>2</sup> /g	Oil Abs, ml/100 g	H <sub>2</sub> O—	X-Ray Analysis, Wt. %					
					Ca	Cl	Fe	Na	Al	Mg
I	9×10 <sup>-6</sup> —7×10 <sup>-5</sup> (0.009-0.07)	133	210	3.46	0.50	0.05	0.12	0.19	0.34	0.01
II	1×10 <sup>-4</sup> —5×10 <sup>-3</sup> (0.1 - 5.0)	80	189	4.58	1.4	0.41	0.40	0.13	0.43	0.22
III	2×10 <sup>-5</sup> —8×10 <sup>-5</sup> (0.02 - 0.08)	102	249	4.72	1.5	0.12	0.09	0.33	0.29	0.21
IV	2×10 <sup>-4</sup> —1×10 <sup>-3</sup> (0.2 - 1.0)	57	263	5.65	1.6	0.55	0.15	0.54	0.28	0.61

\* Predominant Ultimate Particles

+ Water content was determined by measuring weight loss of the sample after heating at 105°C.

The product of Example III was substituted for a conventional precipitated silica filler in a battery separator and the resulting separator was reported to exhibit a reduction in electrical resistance of from 15 to 20 percent.

From the foregoing Examples, it is clear that various procedures and reagents may be used in preparing the hollow silica fillers described herein. Any suitable water soluble alkali metal silicate, for example, serves as a source of the SiO<sub>2</sub> content of the ultimate filler product. Sodium silicate containing from 2 to 4 moles SiO<sub>2</sub> per mole of Na<sub>2</sub>O is the more widely available and used material. Others, including potassium silicate, lithium silicate and sodium potassium silicate containing from 1 to 5 moles of SiO<sub>2</sub> per mole of alkali metal oxide, however, may also be used.

The salt which induces precipitation of the water insoluble siliceous material also can be varied. It is usually preferable that the salt be a water soluble halide, notably a chloride, such as calcium chloride. Among the salts which may be so used include: sodium chloride, barium chloride, strontium chloride, zinc chloride, calcium bromide, sodium iodide, water soluble metal salts of strong acids, i.e., acids having an ionization constant of at least 1 × 10<sup>-2</sup>, such as metal nitrates exemplified by calcium nitrate and sodium nitrate, and metal sulphates such as sodium sulphate.

As with the other reagents, there is latitude in the acidic material used to partially neutralize the aqueous solution of alkali metal silicate. Acids such as hydrochloric acid, sulphuric acid, nitric acid, acetic acid, sulphurous acid, phosphoric acid and carbonic acid (or their anhydrides) can be mentioned. In the main, preference is for acidic materials, the anions of which do not form water insoluble materials under the prevailing conditions with alkali metals.

Acids or acidic materials that may be used in treating the slurry of precipitated water insoluble siliceous material for the purpose of water solubilizing the water insoluble non-siliceous material, such as calcium carbonate may also vary. Most typically, such acids are those which, upon reaction with the aforesaid water insoluble material will provide a water soluble salt of the cation and result in generating an anhydride of the anion of the water insoluble material, such as carbon dioxide when the material is calcium carbonate. For this purpose, strong mineral acids such as hydrochloric, and nitric acids are suggested.

#### CLAIMS

1. A siliceous filler-reinforced microporous polymeric material battery separator wherein the siliceous filler comprises agglomerates of substantially hollow spherical particles of amorphous, precipitated silica having a predominant hollow spherical particle size of between 5 × 10<sup>-6</sup> mm and 5 × 10<sup>-3</sup> mm (between 0.005 and 5.0 microns), the siliceous filler having a surface area of between about 50 and 250 square metres per gram, and an oil absorption of from about 150 to 300 millilitres per 100 grams of filler.

2. A battery separator as claimed in Claim 1, in which between about 10 and about 90 weight percent of siliceous filler, basis the polymeric material, is used to prepare the separator.

3. A battery separator as claimed in Claim 2, in which between about 20 and about 75 weight percent of siliceous filler, basis the polymeric material, is used to prepared the separator.

4. A battery separator as claimed in Claim 3, in which between 30 and 60 weight percent of siliceous

filler, basis the polymeric material, is used to prepare the separator.

- 5 5. A battery separator as claimed in any of Claims 1 to 4, in which the siliceous filler comprises agglomerates of substantially hollow spherical particles having a predominant hollow spherical particle size of between  $1 \times 10^{-5}$  mm and  $1 \times 10^{-3}$  mm (between 0.01 and 1.0 microns), has a surface area of between 75 and 200 square metres per gram, and an oil absorption of from about 200 to 300 millilitres per 100 grams of filler. 5
6. A battery separator as claimed in Claim 5, in which the predominant hollow spherical particle size is between  $1 \times 10^{-5}$  mm and  $2 \times 10^{-4}$  mm (between 0.01 and 0.20 microns) and the oil absorption is from about 230 to 270 millilitres.
- 10 7. A battery separator as claimed in any of Claims 1 to 6, in which the polymeric material is selected from natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, polyisoprene, high molecular weight polyethylene, polypropylene, polybutene, ethylene-propylene copolymers, ethylene-butene copolymers, propylene-butene copolymers, ethylene-propylene-butene copolymers, polyvinyl chloride and vinyl chloride-vinyl acetate copolymers. 10
- 15 8. A siliceous filler-reinforced microporous polymeric material battery separator substantially as hereinbefore described, with particular reference to any of the foregoing Examples. 15
9. A microporous, siliceous filler-reinforced polymeric sheet of a size and configuration adapted to fit between and separate the plates of a battery, the polymeric material of the sheet being selected from natural rubber, styrene-butadiene rubber, polyisoprene, high molecular weight polyethylene, polypropylene, ethylene-propylene copolymers and polyvinyl chloride, the siliceous filler being composed of agglomerates of substantially hollow spherical particles of amorphous, precipitated silica having a predominant hollow spherical particle size of between  $1 \times 10^{-5}$  mm and  $1 \times 10^{-3}$  mm (between 0.01 and 1.0 microns), having a surface area of between 75 and 200 square metres per gram and an oil absorption of from about 200 to 300 millilitres per 100 grams of filler. 20
- 25 10. A polymeric sheet as claimed in Claim 9, in which between 20 and 75 weight-percent of siliceous filler, basis the polymeric material, is used to prepare the polymeric sheet. 25

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